GROWTH OF SILICON THIN FILM BY LPE ON POROUS SILICON BILAYERS

A. Ould-Abbas[1]*, M. Bouchaour[1], N.-E. Chabane-Sari[1], S. Berger[2], A. Kaminski[2] and A. Fave[2]

[1]Laboratoire des Matériaux et Energies Renouvelables, Université de Tlemcen,
BP 119 Tlemcen 13000, Algérie
[2]Laboratoire de Physique de la Matière, UMR-CNRS 5511, Institut National des Sciences
Appliquées de Lyon, Bât. B. Pasc l, 7 avenue Jean Capelle, 69621 Villeurbanne Cedex, France

Abstract

The fabrication of solar cells based on the transfer of a thin silicon film on a foreign substrate is an attractive way to realise cheap and efficient photovoltaic devices. The aim of this work is to realise a thin mono-crystalline silicon film on a double porous silicon layer in order to detach and transfer it on mullite. The first step is the fabrication of a double porous silicon layer by electrochemical anodisation using two different current densities. The low current leads to a low porosity layer and during annealing, the recrystallisation of this layer allows epitaxial growth. The second current leads to a high porosity which permits the transfer on to a low cost substrate. Liquid Phase Epitaxy (LPE) performed with indium (or In+Ga) in the temperature range of 950–1050°C leads to almost homogeneous layers. Growth rate is about 0.35 μm min^{-1}. Crystallinity of the grown epilayer is similar on porous silicon and on single crystal silicon. In this paper, we focus on the realisation of porous silicon sacrificial layer and subsequent LPE growth.

Keywords: *c*-Si, LPE, porous silicon

Introduction

The prices of photovoltaic energy devices have to be decreased to be competitive compared with other low cost ones. About half of the price of photovoltaic silicon modules is due to the silicon wafers. A solution to decrease material cost consists in transferring a thin epitaxial silicon film on to a ceramic or glass substrate [1–5]. In this process, a thin porous silicon sacrificial layer (realised on the top of a silicon wafer) allows epitaxial growth and the removal of the epilayer from the substrate, which can be reused several times. In this study, we report liquid phase epitaxial growth on porous silicon at different temperatures and on different porous silicon samples. Porosity of samples is detected by gravimetry, ellipsometric and gas adsorption measurements. Scanning electron microscope (SEM) analysis have been carried out in order to study *p*-Si evolution *vs.* temperature, LPE layer thickness and morphology.

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*   Author for correspondence: E-mail: a_ouldabbes@mail.univ-tlemcen.dz

Experimental

Porous silicon setup

Porous silicon is made by electrochemical anodisation of monocrystalline silicon in HF/ethanol solution. Ethanol is added to the HF solution in order to improve the wettability of the acid and to allow for the F$^-$ ions to diffuse into the pores, leading to reproducible results.

The anodisation is performed in a double tank cell (Fig. 1) with electrolytic front and back-side contacts separated by the silicon wafer [6, 7]. The two Au electrodes are connected to a current generator. To minimize the effects of hydrogen bubbles formed during the anodisation, an agitator can be placed in the half cell.
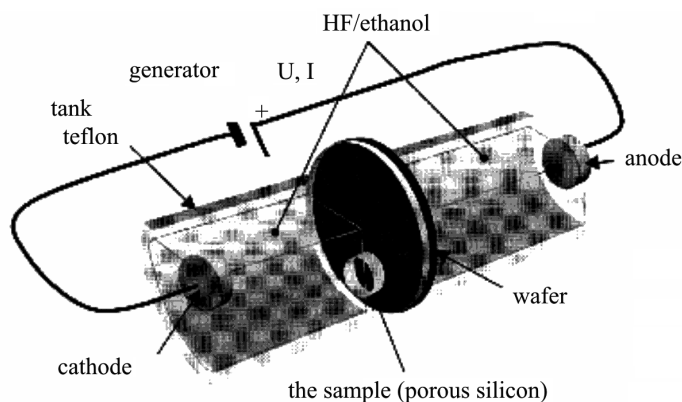
Fig. 1 The anodisation double tank cell with electrolytic front and back-side contacts separated by the silicon wafer

In order to obtain mesoporous silicon (diameter of pores in the range 10–50 nm), we use 0.01 ohm cm^{-1}, boron doped, (100) or (111) Si wafers. Moreover, we adjust the porosity by changing the current density, anodisation time and HF concentration in the solution [8].

Porous silicon monolayers have been realized with a 5 mA cm^{-2} density current and an acid solution of HF(50%) with the following concentration ratio: HF:H$_2$O:C$_2$H$_5$OH (1:1:2). This monolayer has a porosity of around 20% in order to permit epitaxial growth. To allow detachment of the epilayer, we have also made double porous silicon layers with a 20% porosity layer on the surface and a high porosity (>50%) underlayer. To fabricate this high porosity layer, we have changed the current density without changing the solution.

Porosity is evaluated by gravimetric and ellipsometric methods. Ellipsometric measurements are performed from 240 to 700 nm with a 70° angle of incidence. In order to determine the porosity, the Bruggeman approximation [9] is used with a mixture of crystalline silicon and air.

Another advantage of using porous silicon as sacrificial layer is its behaviour under hydrogen annealing. In fact, at high temperatures (like the one used for LPE or VPE), the low porosity layer recrystallises in a QMS (quasi-monocrystalline silicon [2]) layer allowing a high quality epitaxial growth, whereas the high porosity layer transforms in a layer with large voids facilitating the separation.

LPE set-up

The liquid phase epitaxy growth occurs close to the thermodynamic equilibrium and therefore produces high quality epitaxial layers with low density of structural defects and low recombination activity at grain boundaries [10].

It is based on the silicon–metal phase diagram. By cooling a Si-saturated metallic solution, it becomes supersaturated and silicon precipitates on the substrate. In this study we use two different solvents, tin or indium, and two dopants, aluminum or gallium, in order to obtain a *p*-type epilayer. Growth is achieved in a horizontal graphite sliding boat, under palladium-purified hydrogen flow. It usually starts from the saturation temperature (from 930 to 1050°C) and is pursued during a cooling ramp ($0.5°C\ min^{-1}$) down to the final temperature. This cooling rate is a compromise between layer quality and growth rate. Silicon wafers, with sacrificial porous layer, are annealed at 450°C during 15 to 30 min before introduction in the LPE reactor. Then, main annealing of the *p*-Si is realised during the saturation step.

Before contacting *p*-Si with saturated solvent, a supersaturation step can be realised in order to prevent partial dissolution of the porous layer.

Results and discussion

Measurement of the porosity by gravimetric method

The substrates of silicon were weighed before anodisation (m_1), after anodisation (m_2) and after leaving the porous layer by immersion of the wafer in KOH solution (m_3). The porosity is:

$$p=\frac{m_1-m_2}{m_1-m_3}$$

With our experimental conditions, we obtained: $p=24\pm8\%$ for current density $J=5\ mA\ cm^{-2}$ and $p=50\pm8\%$ for $J=75\ mA\ cm^{-2}$ [11].

Measurement of porosity by ellipsometry

In order to determine the porosity, the Bruggeman approximation is used [9] with a mixture of crystalline silicon and air using the relation:

$$(1-p)\frac{\varepsilon_{Si}-\varepsilon_p}{\varepsilon_{Si}+2\varepsilon_p}+p\frac{\varepsilon_0-\varepsilon_p}{\varepsilon_0+2\varepsilon_p}=0$$

with ε_i=permittivity of the element i, obtained by ellipsometric measurements. With our experimental conditions: p=23% for J=5 mA cm^{-2}.

*Measure porosity, cuts pores and surfaces specific by gas adsorption*

This method is based on the determination of the surface of the pores starting from the physical isotherm of adsorption, i.e. the determination of the volume of gas necessary to furnish with a monomolecular layer the totality of porous surface [12]. These measurements made it possible to characterize the layers of strong porosity (J=75 mA cm^{-2}) for which were given:

- the porosity: 48.5%
- the diameter of the pores: 6.9 nm
- surface specifique: 5.36 m^2 g^{-1}

Method study also made it possible to highlight the need for proceeding to a stage of consequent desorption (64 h to primary vacuum 300°C to obtain results convincing).

LPE growth and SE analysis

Concerning the LPE growth on porous silicon monolayers, we first performed experiments at a temperature of 950°C. On (100) porous silicon, a pyramidal layer has been grown (Fig. 2a) and on (111), a 30 μm thick layer has been realised (Fig. 2b) [6, 7, 11]. However, the reproducibility of the experiments was very low and only few layers have been fabricated. This can be attributed to an insufficient recrystallisation of the low porosity layer at this temperature because higher temperatures are usually used to obtain a QMS [2]. Therefore, we increased the annealing temperature to 1050°C and by this way, the reproducibility of the growth was improved on (111) porous silicon. On (100) porous silicon, the epitaxial silicon is still pyramidal because of the high ratio between vertical and lateral growth rate compared with (111) oriented wafer.
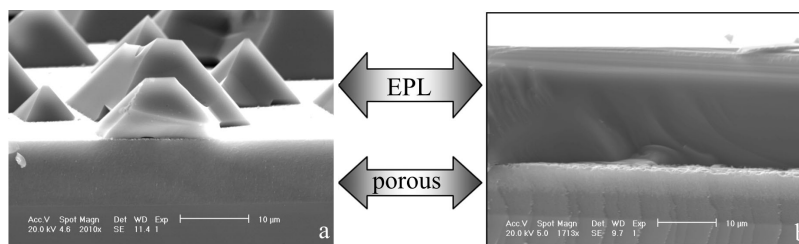
Fig. 2 Cross section SEM view of the LPE growth; a – *p*-Si (100) and b – *p*-Si (111), 20% of porosity

We have also compared epitaxial layers performed with indium or tin solvent but the thickness and the coalescence of the layer is almost similar in both cases.

In order to detach the epilayer from the silicon wafer, the porous silicon bilayer realised with a density current of 5 mA cm^{-2} during 2 min followed by 75 mA cm^{-2} during 30 s, has been analysed (Fig. 3) [13].
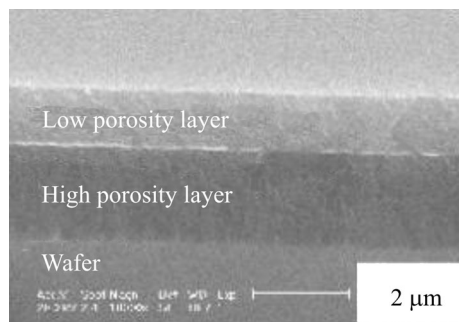
Fig. 3 SEM image of porous silicon bilayer realised with a density current
of 5 mA cm^{-2} during 2 min followed by 75 mA cm^{-2} during 30 s [13]

After annealing at 1050°C, we observed an increase of the low porosity layer surface roughness and of the porosity of the high porosity layer (Fig. 4).

Concerning the liquid phase epitaxial growth of monocrystalline silicon on porous silicon bilayers, we obtained about 25 μm thick layers (Fig. 5) grown at a temperature of 1050°C during 1 h. This corresponds to a growth rate of 0.35 μm min^{-1}. By increasing the LPE growing time, no significant increase of the
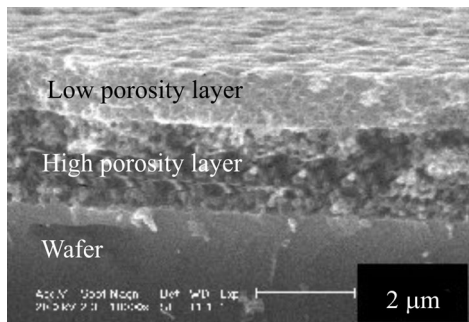

Fig. 4 Same sample as Fig. 3 after annealing at 1050°C [13]

epilayer thickness, nor coalescence (especially for (100) wafers) was observed but this might be due to an insufficient quantity of silicon in the solvent. In order to improve the growing rate, it would be interesting to increase the temperature gradient between the substrate and the solvent [14].

The evolution of the porous silicon with annealing and the coalescence of the epitaxial layer depend strongly on the contamination present in the epitaxial reactor and on the hydrogen flux. For example, porous silicon samples annealed at different places in the reactor (that is, with different exposition to the hydrogen flux, but at the same temperature), transform differently.

Incomplete coalescence is observed on Fig. 5 few holes emerge to the surface. It is probably due to the presence of native oxide on the *p*-Si surface.
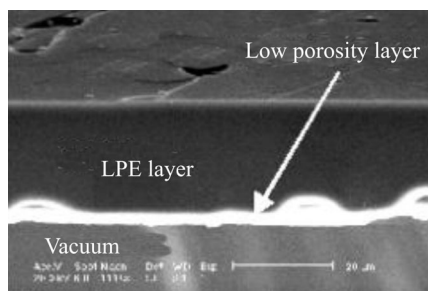
Fig. 5 Cross section SEM view of the LPE growth [13]

We performed also porous silicon annealing at 1050°C and the epitaxial growth at 950°C. However, this has led to a decrease in the coalescence of the epitaxial layer. Similarly, no significant improvement has been observed by annealing porous silicon at 1100°C.
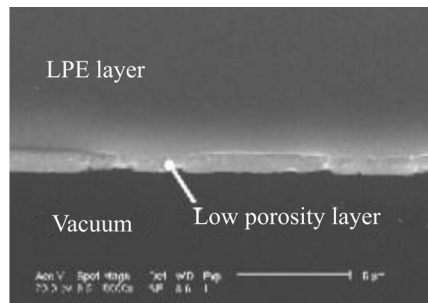
Fig. 6 Cross section SEM view of the LPE growth: zoom on the epilayer and porous silicon interface [13]

The detachment of the epilayer from the substrate is easily obtained mechanically and SEM observations show that the low porosity layer is still 'attached' to the epitaxial silicon (Fig. 6).

Conclusions

In this study, we performed liquid phase epitaxy growth of silicon on porous silicon. During the growth, we analysed the evolution of porous silicon with heat-tratment, epitaxial metal solvent contact and silicon wafers orientation. For both p-Si made on (100) or (111) oriented Si, we observed a crystallization of the porous silicon layer during the treatment. As a consequence, circular holes appeared in the deeper part of the layer. Concerning the growth of silicon on p-Si, pyramids have been observed on (100) oriented wafers whereas a continuous and homogeneous layer has been obtained on (111) p-Si. These different behaviours are due to the presence of the native oxide and different values of lateral growth rate ratio on (100) and (111) oriented p-Si.

Porous silicon growth and liquid phase epitaxy conditions have been varied in order to optimise epitaxy quality and separation. The homogeneity of the layers could be improved by working at higher temperatures than 1050°C. (This was limited by costs). Growing rate is about 0.35 μm min^{-1}.

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